

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Problem Image Mailbox.**

UK Patent Application GB (11) 2 200 906 A
(12) (19) (43) Application published 17 Aug 1988

(21) Application No 8703245

(22) Date of filing 12 Feb 1987

(71) Applicant
Nippon Electric Glass Company Limited

(Incorporated in Japan)

7-1 Seiran 2-chome, Otsu-shi, Shiga-ken, Japan

(72) Inventors

Takehiro Shibuya
Kazuhiro Matsui
Makoto Matsumoto

(74) Agent and/or Address for Service

Mathys & Squire
10 Fleet Street, London, EC4Y 1AY

(51) INT CL
C03C 10/14

(52) Domestic classification (Edition J):

C1M 101 103 115 129 132 133 134 140 141 144
146 150 155 157 159 178 179 214 AA

(56) Documents cited

None

(58) Field of search

C1M
Selected US specifications from IPC sub-class
C03C

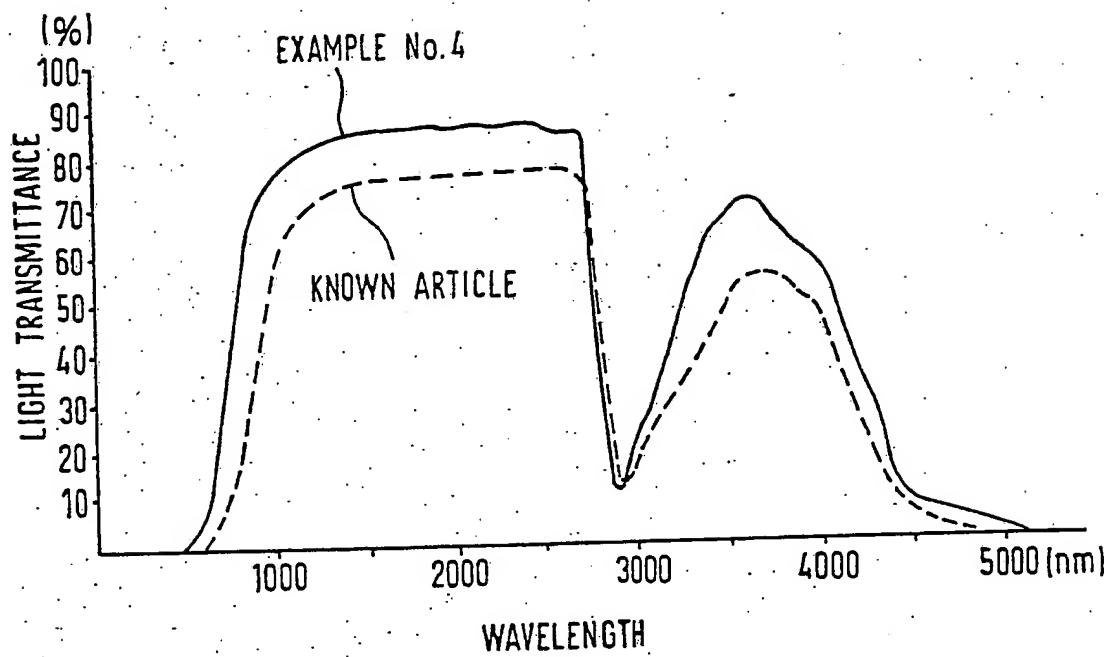
(54) I. R. transparent glass ceramic

(57) An infrared transparent glass ceramic article is useful for top plates of cooking stoves and has a black appearance but an infrared transmittance of about 80% or more for an infrared light of a wavelength 1,500nm, and β -quarts solid solution crystals substantially alone dispersed within glassy matrix without any other crystals. The article consists essentially, by weight, of 60-72% SiO₂, 14-28% Al₂O₃, 2.5-5.5% Li₂O, 0.1-0.9% mgO, 0.1-0.9% ZnO, 3-6% TiO₂, 0.03-0.5% V₂O₅, 0.1-1% Na₂O, 0-1% K₂O, 0-2% CaO, 0-2% BaO, 0-2% PbO, 0-2% As₂O₃, 0-3% ZrO₂ and 0-3% P₂O₅. The article is produced by nucleate in the glass, heating the glass article at a temperature of 650-800°C to forming a desired shape of glass article having the ingredients, heating the glass article at a temperature of 800-950°C to thereby precipitate β -quarts solid solution crystals alone in the glass, and cooling the article to the room temperature.

GB 2 200 906 A

2200906

1/1



2200906

INFRARED TRANSPARENT GLASS CERAMIC ARTICLES

WITH β -QUARTS SOLID SOLUTION CRYSTALS

WITHOUT ANY OTHER CRYSTALS

The present invention relates to infrared transparent glass ceramic articles, and in particular, to such glass ceramic articles useful for top plates of cooking stoves and to a production method thereof.

It is known in the prior art to use a crystallized glass for top plates of cooking stoves.

U.S. patent No. 4,211,820 by Cantaloupe et al discloses such a glass ceramic sheet useful as surfaces for smoothtop cooking stoves which consists essentially, 10. by weight, of 2.5-4.5% Li₂O, 1-2% MgO, 1-2% ZnO, 19.5-21% Al₂O₃, 66.5-68% SiO₂, 4-5% TiO₂, and 0.02-0.2% V₂O₅, the total of these ingredients being 98% or more.

The glass ceramic sheet, in thickness of about 5mm, will display a warm brown coloration and a transmittance of about 20-60% when measured at 800nm.

The glass ceramic sheet is also characterized by 5 a surface layer containing β -quarts solid solution crystals and an interior containing β -spodumene solid solution crystals dispersed within a glassy matrix. The development of these two crystals improves the mechanical strength of the sheet, because the former has 10 a thermal expansion coefficient lower than that of the latter to thereby cause surface reinforcement of the sheet.

However, the development of β -spodumene solid solution crystals tend to unadvantageously cloud the 15 ceramic article white. The white clouded glass ceramic sheet has a problem in appearance and has a reduced infrared transmittance so that a heating element of a cooking stove cannot be observed through the glass ceramic sheet. Therefore, the use of the ceramic sheet 20 for cooking stoves may be unsafe for operators of the stoves.

It is an object of the present invention to provide an infrared transparent glass ceramic article consisting of β -quarts solid solution crystals alone 25 dispersed within a glassy matrix and displaying, in thickness of 3mm, a dark or black appearance, a transmittance of about 5% or less for a visible light of

a wavelength of 500nm or less, and a transmittance of about 80% or more for an infrared light of a wavelength of 1,500nm, as well as having a bending strength of 20,000 psi or more.

5 It is another object of the present invention to provide a method for producing the infrared transparent glass ceramic article.

A glass ceramic articles of the present invention consists essentially, by weight, of 60-72% SiO_2 , 14-28% Al_2O_3 , 2.5-5.5% Li_2O , 0.1-0.9% MgO , 0.1-0.9% ZnO , 3-6% TiO_2 , 0.03-0.5% V_2O_5 , 0.1-1% Na_2O , 0-1% K_2O , 0-2% CaO , 0-2% BaO , 0-2% PbO , 0-2% As_2O_3 , 0-3% ZrO_2 , and 0-3% P_2O_5 . The glass ceramic article has a bending strength of 20,000 psi or more, and consists of 15 β -quarts solid solution crystals alone dispersed within a glassy matrix. The glass ceramic article is characterized by, in thickness of 3mm, a black appearance, a visible light transmittance of about 5% or less for a light of a wavelength of 500nm or less but an 20 infrared transmittance of about 80% for an infrared light of 1,500nm wavelength.

An amount of SiO_2 is limited with a range of 60-72 wt.%. When SiO_2 is below 60%, a thermal expansion coefficient is excessively increased and a mechanical 25 strength is reduced. When SiO_2 is more than 72%, the glass is hardly melted.

Al_2O_3 less than 14 wt.% reduces the chemical resistance of the glass and makes the glass

devitrifyable. When Al_2O_3 exceeds 28 wt.%, the glass is excessively hard and a homogeneous glass cannot be obtained. Therefore, Al_2O_3 is 14 wt.% at minimum and 28 wt.% at maximum.

5 An amount of Li_2O is restricted within a range of 2.5-5.5%. When Li_2O is less than 2.5%, a thermal expansion coefficient is excessively raised and the ceramic becomes cloudy due to development of β -spodumene crystals. When Li_2O is more than 5.5%, devitrification 10 is progressed so that no homogeneous ceramic article can be obtained.

When each of MgO and ZnO is less than 0.1 wt.%, darkness is weakened and the visible light transmittance is increased. Use of more than 0.9 wt.% increases 15 devitrification and generates a white cloud in the ceramic article due to development of β -spodumene crystals, so that the infrared transmittance is lowered.

Use of TiO_2 less than 3 wt.% develops insufficient crystallization, while use of TiO_2 more 20 than 6 wt.% progresses devitrification so that a homogeneous ceramic cannot be obtained.

Li_2O , ZnO and MgO of the above-restricted amounts are important for obtaining the high bending strength of 20,000 psi or more.

25 V_2O_5 is an element for darkening the ceramic articles. In use of V_2O_5 below 0.03 wt.%, a visible light transmittance is unadvantageously increased, and

in use of it above 0.5 wt.%, the infrared transmittance is reduced.

When Na_2O is used below 0.1 wt.%, the ceramic has a numerous crystals precipitated in the surface 5 layer and therefore dissipates the surface brilliance.

Use of more than 1.0 wt.% Na_2O weakens crystallization and excessively increases the thermal expansion coefficient.

In addition to those ingredients SiO_2 , Al_2O_3 , 10 Li_2O_3 , MgO , ZnO , TiO_2 , V_2O_5 , and Na_2O , optional elements of K_2O of up to 1 wt.%, CaO of up to 2 wt.%, BaO of up to 2 wt.%, PbO of up to 2 wt.%, As_2O_3 of up to 2 wt.%, ZrO_2 of up to 3 wt.%, and P_2O_5 of up to 3 wt.% can be contained in the ceramic alone or in combination, 15 inasmuch as the high infrared transmittance is maintained.

Coloring elements such as Fe_2O_3 , MnO , NiO , CoO , Cr_2O_3 , CeO_2 and others should not be added because they reduces the infrared transmittance.

20 The glass ceramic article is produced by forming a desired shape of glass article comprising the above-described ingredients, heating the glass article at a temperature of $650-800^\circ\text{C}$ for a time period sufficient to develop nucleation in the glass, heating 25 the glass article at a temperature of $800-950^\circ\text{C}$ for a time period to develop crystal growth in the glass, to thereby precipitate β -quarts solid solution crystals

alone within a glassy matrix, and cooling the article to the room temperature.

It is important for the high infrared transmittance to strictly control the temperature and 5 the time period in each of the nucleation and crystal growth heating steps. In the nucleation step, nucleation is not normally performed at a heating temperature out of the range of 650-800°C, so that the crystal growth cannot normally be carried out in the 10 subsequent crystallization step.

For the nucleation, the heating temperature is preferably maintained for 0.5-3 hours.

In the crystallization step, use of a heating temperature below 800°C requires an excessive and 15 uneconomical long time period for crystal growth. On heating at a temperature higher than 950°C, β -spodumene crystals develop and the ceramic is, therefore, white cloudy and has a reduced infrared transmittance.

For crystal growth, the heating temperature is 20 preferably maintained for 0.5-5 hours.

A single figure graphically illustrates transmittance-to-wavelength characteristics of a known glass ceramic article and an example of the present invention.

Briefly stating, the present invention attempts to add 0.03-0.5 wt.% V_2O_5 , 0.1-0.9 wt.% ZnO, 0.1-0.9 wt.% MgO, and 0.1-1 wt.% Na₂O in a SiO₂-Al₂O₃-Li₂O glass and 5 to heat-treat the glass for crystallization under a strict temperature and time period control, so as to realize the above-described object.

Ten examples of the present invention are demonstrated in the following Tables 1 and 2. In the 10 Tables 1 and 2, composition of each example is shown together with temperatures and time periods in each heat treatment step, different light transmittance, and a bending strength.

Table I

Ingredients(wt.%)	Examples No.	1	2	3	4	5	
SiO_2	63.0	65.0	69.0	68.0	68.0		
Al_2O_3	26.0	22.3	19.0	20.0	21.0		
Li_2O	5.3	4.6	4.0	5.0	3.0		
MgO	0.1	0.9	0.5	0.5	0.8		
ZnO	0.8	0.1	0.4	0.5	0.5		
TiO_2	4.6	5.7	5.0	4.6	4.8		
V_2O_5	0.1	0.4	0.1	0.1	0.2		
Na_2O	0.1	0.7	1.0	0.2	0.2		
K_2O				0.1	0.5		
CaO							
BaO		0.3					
PbO							
As_2O_5				1.0	1.0	1.0	
ZrO_2							
P_2O_5							
Heat Treating Steps	Nucleation	Temper- ature($^{\circ}\text{C}$)	680	700	720	730	730
		Time period(hr)	2	2	1	2	1
Crystal Growth		Temper- ature($^{\circ}\text{C}$)	800	850	850	850	870
		Time period(hr)	2	1	1	1	1
Trans- mittance (%)	500nm (Visible light)	1	0	0	0	0	
	1500nm (Infrared light)	83	81	88	85	85	
Bending Strength (psi)		35500	54000	42600	64000	56800	

Table 2

Examples No.		6	7	8	9	10	
Ingredients(wt.%)							
SiO ₂		66.0	66.0	66.0	66.0	65.5	
Al ₂ O ₃		22.0	22.0	22.0	22.0	22.0	
Li ₂ O		4.2	4.2	4.2	4.2	4.2	
MgO		0.5	0.5	0.5	0.5	0.8	
ZnO		0.5	0.5	0.5	0.5	0.1	
TiO ₂		4.2	4.2	4.2	3.2	3.9	
V ₂ O ₅		0.1	0.1	0.1	0.1	0.05	
Na ₂ O		0.5	0.5	0.5	0.5	0.4	
K ₂ O						0.25	
CaO		1.0				1.5	
BaO			1.0				
PbO				1.0			
As ₂ O ₅		1.0	1.0	1.0	1.0	1.3	
ZrO ₂					1.0		
P ₂ O ₅					1.0		
Heat Treating Steps	Nucleation	Temper- ature(°C)	720	720	720	700	700
		Time period(hr)	2	2	2	3	2
Crystal Growth	Temper- ature(°C)	850	850	900	850	870	
	Time period(hr)	1	1	1	2	1	
Trans- mittance (%)	500nm (Visible light)	0	0	0	0	2	
	1500nm (Infrared light)	85	86	84	82	90	
Bending Strength (psi)		42600	45400	42600	64000	45000	

Those examples in the Tables 1 and 2 were produced by the following processes.

Raw materials, which are in states of oxide, hydroxide, halide, carbonate, nitrate, or others, were measured to form a batch, which, when melted together, will be converted into the desired oxide in each proper proportion as shown in the Tables 1 and 2. The batch ingredients were mixed together uniformly, and were melted in a platinum crucible within an electric furnace at a temperature of 1550-1620°C for 16 hours. A glass rod of about 5mm. in diameter was drawn from the molten glass, and the remainder of the molten glass was poured onto a carbon plate to form a glass plate of about 4mm in thickness using a stainless steel roll. Both were slowly cooled to the room temperature in an annealing furnace. The cooled glass rod was cut to form a sample rod of a 50mm length and the cooled glass plate was also cut to obtain a plate sample of 50 x 50 x 4mm.

Those rod and plate samples were loaded in an electric furnace with a heating temperature being elevated at a rate of 300°C/hour from the room temperature to the nucleation temperature range. The rod and plate samples were maintained at a nucleation temperature for a nucleation time period as described in the Tables 1 and 2. Then, the temperature was elevated at a rate of 80°C/hour to a crystal growth temperature and maintained at the crystal growth temperature for a crystal growth time period as described in the Tables 1

and 2, and thereafter, were slowly cooled to the room temperature.

The resultant rod and plate glass ceramic samples were observed to have a dark or black and brilliant appearance without any white cloud and a smooth surface.

The rod sample was subjected to a conventional three-point bending test. Bending strength of 35,500-64,000 psi was measured for the examples as 10 described in the Tables 1 and 2.

The plate sample was polished to become about 3mm in thickness and was subjected to a measurement of transmittance by use of a spectrophotometer. A transmittance was measured about 80% or more for an 15 infrared light of a 1500nm wavelength, but a visible light transmittance was almost 0%, as shown in the Tables 1 and 2.

The single figure illustrates light transmittance-to-wavelength characteristics of example 20 No. 4 of the present invention and a known glass ceramic article.

The known glass ceramic articles consisted, by weight, of 67.5% SiO_2 , 20.0% Al_2O_3 , 4.1% Li_2O , 17.5% MgO , 1.25% ZnO , 4.5% TiO_2 , 0.1% V_2O_5 , 0.2% Na_2O , 0.1% 25 K_2O , and 0.5% As_2O_3 , and was produced by processes similar to the examples of the present invention.

It was appreciated from analysis of crystalline structure that the example of the present invention

consisted of β -quarts solid solution crystals alone dispersed in a glassy matrix while the known glass ceramic having β -spodumene crystals in addition to β -quarts solid solution crystals.

5 It was also observed that the example of the present invention displays a uniformly black appearance but the known ceramic having a white cloud.

The figure shows that the example of the present invention has an infrared transmittance higher than that
10 of the known glass ceramic.

CLAIMS:

1. An infrared transparent glass ceramic article having a bending strength of 20,000 psi or more, displaying, in thickness of about 3mm, a transmittance of about 5% or less for a visible light of a wavelength of 500nm or less but a transmittance of about 80% or more for an infrared light of a wavelength of 1,500nm, and a dark or black appearance, and consisting of a glassy matrix and β -quarts solid solution crystals substantially alone dispersed within the glassy matrix,
10 said glass ceramic article consisting essentially, by weight, of 60-72% SiO_2 , 14-28% Al_2O_3 , 2.5-5.5% Li_2O , 0.1%-0.9% MgO , 0.1-0.9% ZnO , 3-6% TiO_2 , 0.03-0.5% V_2O_5 , 0.1-1% Na_2O , 0-1% K_2O , 0-2% CaO , 0-2% BaO , 0-2% PbO , 0-2% As_2O_3 , 0-3% ZrO_2 , and 0-3% P_2O_5 .
2. A method for producing an infrared transparent glass ceramic article having a bending strength of 20,000 psi or more, displaying in thickness of about 3mm, a transmittance of about 5% or less for a visible light of a wavelength of 500nm or less, but a transmittance of about 80% or more for an infrared light of a wavelength of 1,500nm, and a dark or black appearance, which comprises steps of:
forming a desired shape of glass article
10 consisting essentially, by weight, of 60-72% SiO_2 , 14-28% Al_2O_3 , 2.5-5.5% Li_2O , 0.1-0.9% MgO , 0.1-0.9% ZnO ,

(Claim 2 continued)

3-6% TiO_2 , 0.03-0.5% V_2O_5 , 0.1-1% MgO , 0-1% K_2O , 0-2%
CaO, 0-2% BaO, 0-2% PbO, 0-2% As_2O_3 , 0-3% ZrO_2 , and 0-3%
 P_2O_5 ;

15 heating the glass article at a temperature of
650-800°C for a time period sufficient to nucleate in
the glass;

heating the glass article at a temperature of
800-850°C for a time period sufficient to develop
20 crystal growth in the glass, to thereby precipitate
substantially β -quarts solid solution crystals alone in
the glass; and

cooling the article at the room temperature.

3. An infrared transparent glass ceramic article
25 substantially as hereinbefore described and exemplified.

4. A method for producing an infrared transparent
glass article substantially as hereinbefore described and
exemplified.